Endex stabilization of thermally unstable and explosive liquid phase systems

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ABSTRACT:
In Endex coupling of reactive systems an exothermic reaction is directly coupled to an endothermic reaction. This work demonstrates the potential of Endex storage systems for safe storage of explosive and dangerous substances. Rigorous criteria are derived for which thermal runaway is forbidden in an Endex storage system, which is thus intrinsically safe. For several industrial organic peroxides that undergo exothermic thermal decomposition, endothermic reaction partners are chosen from hydrated metal salts that undergo endothermic dehydrations. Thermokinetic data from the literature are used to test Endex stabilization of these systems numerically. It is found that Endex stabilization is successful for periods of at least one week even when therokinetic matching is not ideal. Some of the difficulties of Endex stabilization of peroxides thaat undergo multistage decomposition are highlighted.

KEY WORDS: Endex · Thermal runaway · Thermal stabilization · Organic peroxides

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1 Introduction

An Endex thermoreactive system in general consists of an exothermic reaction that is directly coupled thermally and kinetically with an endothermic reaction (Gray and Ball 1999) (see section 2). In this work the potential of Endex-designed storage systems for energetic unstable liquids, in particular, for industrial organic peroxides, is investigated, and several Endex reaction couples are characterised in numerical simulation.

Endex theory originally was applied to the continuous-flow strirred tank reactor (CSTR), but may be adapted to thermo-reaction systems of any type. Storage tanks in which an undesirable exothermic reaction occurs resemble batch reactors rather than CSTRs, although it is certainly possible for CSTR-like behaviour to occur locally within a large storage tank (Ball 2011). Unlike a dedicated batch reactor though, storage tanks are not usually actively monitored and controlled. An exothermic reaction that sets in — perhaps due to contamination with a substance that acts as a catalyst — may be undetected until the tank vents, ruptures or explodes.

Even when the temperature is continuously monitored, a rise in temperature inside the storage tank may not be sensed, because the heat of reaction is absorbed by excitation of the intermolecular vibrational modes and intramolecular rotational modes of the liquid. Violent thermal runaway occurs when these modes are saturated, even though almost no increase in temperature is recorded beforehand. Energetic liquids, with their high specific heat capacity and therefore numerous internal modes and limited translational modes, may undergo thermal runaway via a violent oscillatory instability rather than via classical (Semenov) ignition (Ball 2013b).

One can readily appreciate the need for thermal control of batch storage systems by design rather than palliation, and this is the philosophy behind Endex systems.

The focus in this work is on evaluating Endex storage for liquid or solvated organic peroxides. These substances are widely used in the polymer industry and as bleaching and disinfectant agents, and are manufactured, stored and transported in vast quantities. (For example, Tseng et al. (2007) claim that in 2004 the annual usage of methyl ethyl ketone peroxide (MEKP) was 13,000 tonnes in China alone.) However, when heated or contaminated with a catalytic substance they can undergo explosive decomposition, with or without partial oxidation of the products. Non-diluted peroxides contain so much energy that under runaway conditions the temperature rise will become uncontrollable before a conversion of 10% (Hordijk and de Groot 1986). Serious and fatal thermal explosion accidents in industry involving peroxides are unacceptably common. Ho and Duh (1998) tabulated data on 10 thermal runaway incidents involving peroxides that occurred in Taiwan between 1979 and 1998, which caused a total of 56 fatalities and 198 serious injuries. Six of these were storage tank explosions. Graham et al. (2011) lists 18 significant incidents from 1953 to 2007 involving explosions of MEKP resulting in a total of 102 fatalities and 332 injuries.

Two possible configurations for an Endex storage system are sketched in figure 1. In (a) separate modules housing the potential exothermic and endothermic reactions are arranged so that thermal contact is optimal. In

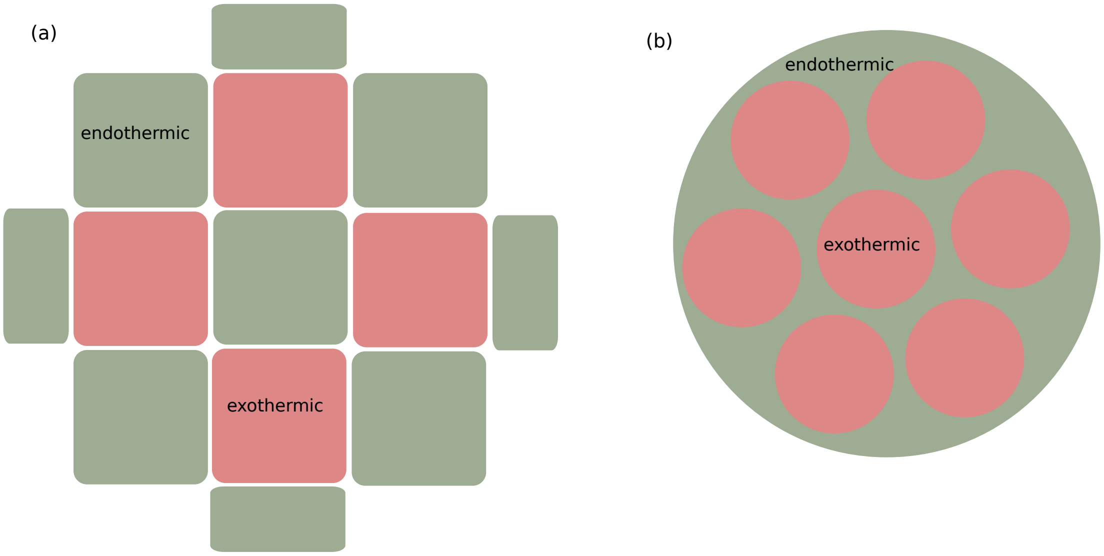

Figure 1. Two designs for an Endex storage system.

(b) a number of containers housing the potential exothermic reaction are set inside a bath containing a substance that is capable of endothermic reaction. The design (a) is presumably more expensive than (b) but may offer advantages in terms of easy modular scaleability, and it could be a preferred design for transportation of large quantities of thermally hazardous substances. The design (b) may be more suitable for economical on-site storage, where containers may be tapped and re-filled, or removed and replaced, as required.

2 Endex theory and batch model

Endex theory and principles were introduced by Gray and Ball (1999) and Ball and Gray (1999) in the context of building intrinsic thermal stability into chemical reactors housing exothermic reactions, concomitantly recovering the reaction heat directly in the bonds of the endothermic reaction product. An Endex-configured system can be thought of as a reactor that is cooled by endothermic reaction rather than by inert coolant, thus the cooling rate is exponential rather than linear and the reactions 'see' and respond to each other in real time. The effect on the temperature is illustrated qualitatively in figure 2, for hypothetical reactions in a continuous-flow stirred tank reactor (CSTR). In the conventionally cooled reactor (a) the heat removal rate is linear with respect to the temperature and in this case the high conversion steady state occurs at 1100 K. In the Endex reactor (b) the heat removal rate has a strong exponential component and the temperature of the high conversion steady state is lower by 23%, all other things being equal. The potential of Endex processes in terms of improved safety can be appreciated, and operating cost savings have been assayed quantitatively for a particular Endex process (Ball 2013a).

Here we model the simplest Endex storage system as a well-stirred batch reactor comprising segment 1, housing an exothermic reaction, in good thermal contact with segment 2, housing an endothermic reaction. It is both convenient and instructive to work with dimensionless quantities. Accordingly, the model may be expressed as the following dimensionless dynamical mass and enthalpy conservation equations:

$$\frac{\mathrm{d}x_1}{\mathrm{d}\tau} = -x_1^n \mathrm{e}^{-1/u_1} \tag{1}$$

$$\varepsilon_1 \frac{\mathrm{d}u_1}{\mathrm{d}\tau} = x_1^n \mathrm{e}^{-1/u_1} - \ell_{\mathrm{ex}}(u_1 - u_2) + \ell_{\mathrm{d}}(u_{\mathrm{a}} - u_1) \tag{2}$$

$$\frac{\mathrm{d}x_2}{\mathrm{d}\tau} = -x_2^m \nu \mathrm{e}^{-\mu/u_2} \tag{3}$$

$$\gamma\varepsilon_2 \frac{\mathrm{d}u_2}{\mathrm{d}\tau} = -\gamma\alpha x_2^m \nu \mathrm{e}^{-\mu/u_2} + \ell_{\mathrm{ex}}(u_1 - u_2). \tag{4}$$

The initial conditions are $x_1(\tau = 0) = x_2(\tau = 0) = 1$, $u_1(\tau = 0) = u_2(\tau = 0) = u_0$. Equations (1)–(4) describe

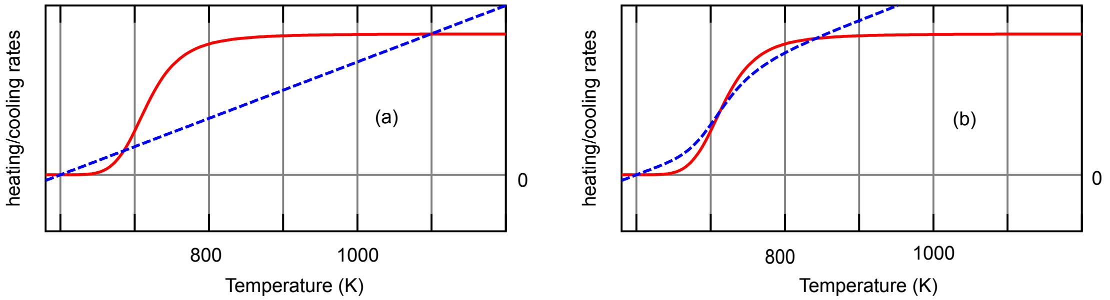

Figure 2. Linear (a) versus nonlinear (b) cooling of a reactor. Solid lines represent reactive heating rates, dashed lines represent cooling rates.

two well-stirred, thermally coupled segments, each running a single reaction. Notation and symbols are defined in Table 1. In the following analysis we will set the reaction orders n and m equal to 1. As we will see, the thermal decomposition of most peroxides is observed to be first order, despite the complexity of the process in terms of elementary reactions. The selected endothermic reaction are also first order empirically.

Table 1. Nomenclature.

Symbol	Definition (units)	Symbol	Definition (units)
A	pre-exponential factor (s^{-1})	L	thermal conductance (W/K)
c	concentration of substance (mol/kg)	M	mass of segment contents (kg)
C	specific heat capacity (J/(kg K)	R	gas constant
E	activation energy (J/mol)	t	time (s)
ΔH	reaction enthalpy (J/mol, J/g)	T	temperature (K)
Dimensionless groups			
ℓ	$LE_1/(c_{1,0}M_1A_1(-\Delta H_1)R)$	ε	$CE_1/(c_{1,0}(-\Delta H_1)R$
x	c/c_0	μ	E_2/E_1
u	RT/E_1	ν	A_2/A_1
α	$(-\Delta H_2)c_{2,0}/((-\Delta H_1)c_{1,0})$	τ	tA_1
γ	M_2/M_1		
Subscripts			
0	initial value	a	of the ambient temperature
1	of the exothermic reaction	d	of heat loss to the environment
2	of the endothermic reaction	ex	of heat exchange between segments

3 Endex storage — results

3.1 Some useful bounds

For an effective storage system, we are interested in defining conditions for which the thermal stability of this system is guaranteed. To obtain some bounds on the thermal behaviour we first apply the ideal Endex approximations,

(i) adiabaticity, or the limit $\ell_{\mathrm{d}} \to 0$, and

(ii) perfect thermal coupling between the segments, or $\delta \equiv 1/\ell_{\mathrm{ex}} \to 0$,

to the system defined by Eqs (1)–(4). Condition (i) renders the system integrable: summing Eqs (1)–(4) with $\ell_{\mathrm{d}} = 0$, $m = n = 1$ gives $\mathrm{d}/\mathrm{d}\tau\,[x_1 + \varepsilon_1 u_1 - \gamma\alpha x_2 + \gamma\varepsilon_2 u_2] = 0$, from which

$$[x_1 + \varepsilon_1 u_1 - \gamma\alpha x_2 + \gamma\varepsilon_2 u_2] = [1 + \varepsilon_1 u_0 - \gamma\alpha + \gamma\varepsilon_2 u_0]\,. \tag{5}$$

Multiplying Eq. (4) through by δ and taking the limit $\delta \to 0$ gives $u_1 = u_2 \equiv u$. We shall use Eq. (5) to define x_2 in terms of x_1 and u, and work with the resulting reduced dynamical system,

$$\frac{\mathrm{d}x_1}{\mathrm{d}\tau} = -x_1 \mathrm{e}^{-1/u} \tag{1}$$

$$(\varepsilon_1 + \gamma\varepsilon_2)\frac{\mathrm{d}u}{\mathrm{d}\tau} = x_1 \mathrm{e}^{-1/u} - \gamma\alpha x_2 \nu \mathrm{e}^{-\mu/u} \tag{6}$$

$$\gamma\alpha x_2 = \gamma\alpha - 1 + x_1 - (\varepsilon_1 + \gamma\varepsilon_2)(u_0 - u). \tag{7}$$

Let us define the *perfect matching* case as the hypothetical system for which $\alpha\gamma = \nu = \mu = 1$. In this case the system has the exact solution, $u = u_0, x_1 = x_2 = \exp -tz$, where $z = \exp 1/u_0$. This perfect matching solution is not interesting in itself, since it applies to an Endex reaction couple that may not exist. Its importance is that it defines the upper bound of the dynamical temperature $u(\tau)$ for a wide range of thermokinetically mismatched, real reactions, as shown by the following analysis.

In general, for non-perfect matching reaction couples we can write $u = u_0 + \theta$, where θ is now the dependent variable, and Eqs (1), (6) and (7) become

$$\frac{\mathrm{d}x_1}{\mathrm{d}\tau} = -x_1 \mathrm{e}^{-1/(u_0+\theta)}$$

$$(\varepsilon_1 + \gamma\varepsilon_2)\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = x_1 \mathrm{e}^{-1/(u_0+\theta)} - \gamma\alpha x_2 \nu \mathrm{e}^{-\mu/(u_0+\theta)}$$

$$\gamma\alpha x_2 = \gamma\alpha - 1 + x_1 + (\varepsilon_1 + \gamma\varepsilon_2)\theta$$

We can see by inspection that where $\gamma\alpha > 1$ (thermal mismatching favours the endothermic effect) then $x_2 > x_1$. If also $\nu > 1, \mu < 1$ (kinetic mismatching favours the endothermic reaction) then $\mathrm{d}\theta/d\tau < 0$ for all time. This important result may be expressed as follows:

$$u(\tau) \leq u_0 \quad \forall \quad \gamma\alpha \geq 1, \nu \geq 1, \mu \leq 1. \tag{8}$$

The ineqality relations (8) state that there is a defined, broad range of thermokinetic parameter values over which the ideal Endex batch system remains free of thermal excursions for all time. A similar result was obtained rigorously for an Endex CSTR system by Gray and Ball (1999), using a comparison theorem on differential inequalities.

Returning to the ideal Endex system modelled by Eqs (1), (6) and (7), we may also make use of the maximum adiabatic temperature $u_{\max}$ of the system. Two more useful bounds may be distinguished:

1. Gross kinetic mismatching: For ν and/ or $\mu \gg 1$ the exothermic conversion is largely complete before the endothermic reaction has begun. Thus for $x_2 \approx 1, x_1 \approx 0$ we obtain

   $$u_{\max}(\text{mis}) = u_0 + \frac{1}{\varepsilon_1 + \gamma\varepsilon_2}. \tag{9}$$

   For ν and/ or $\mu \ll 1$ the reverse situation may occur: the endothermic conversion is largely complete before the exothermic reaction has begun. Initially the temperature falls to a minimum at $x_1 \approx 1, x_2 \approx 0$:

   $$u_{\min}(\text{mis}) = u_0 - \frac{\gamma\alpha}{\varepsilon_1 + \gamma\varepsilon_2}.$$

   However, with no endothermic reactant present after this, the temperature would climb to $u_{\max}(\text{mis})$, Eq. (9), as the exothermic reaction takes over.

2. Kinetic matching, where $\nu = \mu = 1$: In this case enthalpy balance is freed from explicit dependence on the conversion:

   $$(\varepsilon_1 + \gamma\varepsilon_2)\frac{\mathrm{d}u}{\mathrm{d}\tau} = \mathrm{e}^{-1/u}\left[1 - \gamma\alpha - (\varepsilon_1 + \gamma\varepsilon_2)(u - u_0)\right].$$

   The non-trivial temperature extremum is

   $$u_{\max}(\text{mat}) = u_0 + \frac{1 - \gamma\alpha}{\varepsilon_1 + \gamma\varepsilon_2}. \tag{10}$$

Thus, for $\nu = \mu = 1$ and $\gamma\alpha \geq 1$ we have $u(\tau) \leq u_0$. The dimensionless group $\gamma\alpha$ represents the absolute enthalpy effect. In this case the enthalpy effect of the endothermic reaction is greater than that of the exothermic reaction. For $\nu = \mu = 1$ and $\gamma\alpha < 1$ we have $u(\tau) < u_{\max}(\text{mat})$, Eq. (10), and the enthalpy effect of the exothermic reaction dominates. With respect to the design of safe Endex storage systems this result means that, provided the reactions are kinetically well-matched, the system will evolve towards the known temperature maximum.

More generally, for a moderate degree of kinetic mismatching, the temperature would evolve to a maximum that is between $u_{\max}(\text{mat})$, given by Eq. (10), and $u_{\max}(\text{mis})$, given by Eq. (9).

To what extent can the inequalities (8) and the ideal Endex conditions (i) and (ii) be realized in practice, in a storage tank situation? The thermal effect group $\gamma\alpha$ can be controlled by system design, by setting the compartment volume ratio, judicious selection of Endex reaction pairs and selecting the initial concentrations of the reactants. (See definitions of the dimensionless groups in Table 1.) The kinetic parameters ν and μ are fixed by selection of the reaction pair, and by experimentation may be manipulated by use of catalysts and inhibitors. The adiabatic condition $\ell_{\mathrm{d}} \to 0$ is easily approximated by using sufficient thermal lagging. In some cases it may be possible to mix the endothermic and exothermic reactants in the same container, but where there is a physical partition the ideal condition $\delta = 0$ cannot be achieved, since that would require infinite heat transfer area. Although very good thermal conductance between the segments is technically achievable, it would be helpful to gain some insights into the system behaviour for finite thermal conductance.

Let us use Eq. (5) to define u_2 in terms of u_1, x_1 and x_2. Our system is then

$$\frac{\mathrm{d}x_1}{\mathrm{d}\tau} = -x_1 \mathrm{e}^{-1/u_1} \tag{1}$$

$$\frac{\mathrm{d}x_2}{\mathrm{d}\tau} = -x_2 \nu \mathrm{e}^{-\mu/u_2} \tag{3}$$

$$\varepsilon_1 \frac{\mathrm{d}u_1}{\mathrm{d}\tau} = x_1 \mathrm{e}^{-1/u_1} - \ell_{\mathrm{ex}}(u_1 - u_2) \tag{11}$$

$$\gamma\varepsilon_2 u_2 = 1 - x_1 - \gamma\alpha(1 - x_2) + (\varepsilon_1 + \gamma\varepsilon_2)u_0 - \varepsilon_1 u_1. \tag{12}$$

For highly exothermic reactions (such as thermal decomposition of most organic peroxides) we define the 'fast' timescale $\tau' \equiv \tau/\varepsilon_1$ and recast the system in terms of this new dependent variable:

$$\begin{aligned}\frac{\mathrm{d}x_1}{\mathrm{d}\tau'} &= -\varepsilon_1 x_1 \mathrm{e}^{-1/u_1}\\ \frac{\mathrm{d}x_2}{\mathrm{d}\tau'} &= -\varepsilon_1 x_2 \nu \mathrm{e}^{-\mu/u_2}\\ \frac{\mathrm{d}u_1}{\mathrm{d}\tau'} &= x_1 \mathrm{e}^{-1/u_1} - \ell_{\mathrm{ex}}(u_1 - u_2)\end{aligned}$$

For $\varepsilon_1 \to 0$ we have $x_1 \approx x_2 \approx 1$ and $u_2 \approx u_0$. Physically this simply means that on the 'fast' timescale the exotheric segment can heat up before the endothermic segment has time to respond. On this 'fast' timescale, then, the temperature evolves approximately as

$$\frac{\mathrm{d}u_1}{\mathrm{d}\tau'} = \mathrm{e}^{-1/u_1} - \ell_{\mathrm{ex}}(u_1 - u_0) \tag{13}$$

Equation (13) is identical to the temperature equation of classical thermal explosion (Semenov) theory. It tells us that in this regime the thermal stability is determined by the slope of the linear heat loss rate, i.e., by ℓ_{ex}. This balancing act, between the nonlinear heat generation rate $r_{\mathrm{h}} \equiv \exp(-1/u_1)$ and the linear cooling rate $r_{\mathrm{c}} \equiv \ell_{\mathrm{ex}}(u_1 - u_0)$, is shown graphically in Fig. 3. Critical tangency conditions are solutions of

$$G \equiv \mathrm{e}^{-1/u_1} - \ell_{\mathrm{ex}}(u_1 - u_0) = 0, \quad G_u \equiv \frac{\partial}{\partial u_1} G = 0,$$

which evaluate to two points,

$$u_1 = \frac{1}{2}\left(1 \pm \sqrt{1 - 4u_0}\right), \quad \ell_{\mathrm{ex}} = \frac{4\exp\left(\frac{2}{1 \pm \sqrt{1-4u_0}}\right)}{\left(1 \pm \sqrt{1 - 4u_0}\right)^2}$$

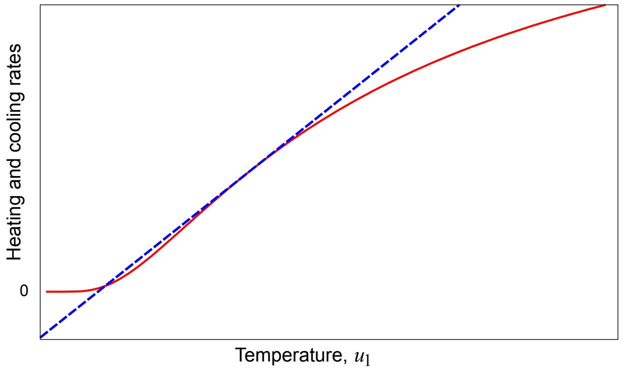

Figure 3. The nonlinear heat generation rate r_h (solid line) and the linear cooling rate r_c (dashed line) from Eq. (13) are plotted against u_1. In this example the slope of r_c, l_ex, is equal to the critical upper tangency value.

The Semenov approximation applies for $u_0 \leq 1/4$, and we are interested in the upper critical value of ℓ_ex. Within the Semenov approximation, then, we can say that thermal stability is assured for

$$\ell_\mathrm{ex} > \frac{4\exp\left(\frac{2}{1+\sqrt{1-4u_0}}\right)}{\left(1+\sqrt{1-4u_0}\right)^2}. \tag{14}$$

As a numerical example, fixing $T_0 = 293\,\mathrm{K}$ and a typical $E_1 = 120\,\mathrm{kJ/mol}$ gives $u_0 = 0.020$, and from Eq. (14) the upper critical value of $\ell_\mathrm{ex} = 0.375$.

Returning to ‘normal’ time τ in Eqs (1), (3) and (11), for $\varepsilon_1 \to 0$ we have

$$0 \approx x_1 \mathrm{e}^{-1/u_1} - \ell_\mathrm{ex}(u_1 - u_2),$$

and the reactive heat release rate $r_\mathrm{hr} \equiv x_1 \mathrm{e}^{-1/u_1} <$ the ‘fast’ time heat release rate r_h because $x_1 < 1$. Consequently the inequality condition (14) also assures the stability of the system when reactant is consumed.

We can simplify the condition (14) further. Taking a power series expansion of the right hand side of the inequality (14) in u_0 around $u_0 = 0$ we find

$$\ell_\mathrm{ex} > \frac{1}{\mathrm{e}} + \frac{u_0}{\mathrm{e}} + \frac{3u_0^2}{2\mathrm{e}} + \frac{17u_0^3}{6\mathrm{e}} + \ldots$$

For $u_0 \lessapprox 0.05$ this may be truncated safely to the first two terms, which gives the following simple rule of thumb for thermal stability of the system described by Eqs (1), (3), (11) and (12)

$$\ell_\mathrm{ex} > \mathrm{e}^{-1}(1 + u_0). \tag{15}$$

The conditions (8) are based on an idealization, condition (14) is based on an idealization and an approximation, and condition (15) is an approximation based on an idealization and an approximation. Nevertheless, they are useful because the approximations used are often valid for the highly energetic reactive liquids we are considering, and the idealisations can be approached by design.

3.2 Choice of endothermic reactants

Criteria for selection of an endothermic reactant for an Endex storage system are quite different from those one would use for an Endex reactor. For the latter, the endothermic reaction product is a saleable commodity; for the former it is not. Therefore, the endothermic substance must be cheap. It should be stable at the storage temperature for the duration of storage, which might be days to months, and its reaction products should be non-toxic.

Hydrates of low-cost metal salts would seem to have the qualities needed. Hydrated minerals salts, particularly sulfates, are abundant and widespread in the lithosphere of the earth. In the temperature range of interest (∼290–400 K) the only reaction product (in most cases) is water vapor, since the anyhdrous salt decomposes at much higher temperatures. *Therefore an important safety consideration is that pressure-venting of the endothermic segment must be provided,* since hot steam may be produced.

A collection of thermokinetic and thermochemical data from the literature for metal salt dehydration reactions is given in Table A1. Polyhydrous salts typically dehydrate in stages as the temperature rises, the last water molecule often being released at a significantly higher temperature than those of the penultimate dehydration. In this respect such mineral salt hydrates may be particularly suited to pair with organic peroxides, many of which also undergo staged thermal decompositions.

This brings us to an important concern when pairing endothermic and exothermic reations in an Endex system: an endothermic reaction should be chosen that suppresses the lowest temperature exothermic reaction of a substance that undergoes sequential thermal decompositions. Many thermogenic substances can undergo a low activation energy, exothermic reaction which heats the system to the point where the main high activation energy, explosive reaction kicks in. However it is the low activation energy reaction that is actually responsible for the explosive thermal decomposition. Gray and Macaskill (2004) pointed out this fact with respect to the explosive thermal decomposition of calcium hypochlorite, and also that the low activation energy reaction in such two-stage decompositions is often not detected in DSC runs to determine activation energy.

3.3 Best-matching Endex pairs

Literature data for the decomposition of industrial peroxides are collected in Table A2. A number of potential 'best matched' Endex couples were selected from Tables A1 and A2, and listed in Table 2 with numerical values of the dimensionless parameters ν, μ, α, ε_1, ε_2 and ℓ_{ex}. The values of γ_{min} listed are the minimum values of γ required for the product $\gamma\alpha$ to equal 1. γ is an adjustable parameter by design.

Table 2. 'Best-matching' Endex rection couples selected from Tables A1 and A2.

# (Table A2)	# (Table A1)	ν	μ	α	γ_{min}	ε_1	ε_2	ℓ_{ex}
1.1c	2.3	1.10	0.809	4.05	0.247	83.3	63.5	0.375
1.2c	2.11	3.3	1.01	0.974	1.03	47.8	36.4	0.376
1.4c	2.5	3.03	1.01	3.29	0.30	117.7	89.7	0.374
1.5d	2.9	0.63	0.955	0.59	1.70	28.0	21.3	0.374
1.6	2.7	124	1.01	0.72	1.38	25.5	19.4	0.375
1.7b stage I	2.10 stage I	0.37	0.91	1.07	0.93	551.9	420.5	0.386
1.7b stage II	2.11	0.07	1.00	0.642^{a}	0.93	551.9	420.5	0.386
1.7b stage III	2.2	1.33	0.95	0.778^{a}	0.93	551.9	420.5	0.386

$^{a}\Delta H_2/\Delta H_1$.

In some cases, widely different kinetic parameters are reported by different groups for the same substance. No doubt this is largely due to experiment-specific factors, because I have every confidence in the accuracy of the raw experimental measurements. However, in most cases the kinetic parameters were determined by processing the data from DSC scans, apparently without checking that the assumption of a spatially uniform sample temperature is valid. If this assumption is not valid the activation energy can be over-estimated. A discussion of this problem and conditions for validity are given in Gray and Macaskill (2004). In a real Endex storage system an overestimate of the activation energy of the exothermic reaction could lead to failure of purpose, because an endothermic reaction could be chosen to match the ficticious high activation energy of the exothermic reaction and the reactions may not 'see' each other.

The specific heat of an unspecified mixed solid metal salt hydrate was determined to be 1524 J/(kg K) by Căilean et al. (2011), and this is the value used for C_2 in the computations. The specific heat of a typical organic peroxide of 2000 J/(kg K) (Kotoyori 1995) was the value used for C_1 in the computations. For the values of ℓ_{ex} we apply the rule of thumb, Eq. 15 with $T_0 = 293\,\text{K}$.

The performances of the first five Endex pairs in Table 2 are discussed in turn as follows, with reference to the integrated time traces over a one week period in shown Fig. 4:

- # 1.1c and # 2.3: For this pair the inequality relations (8) are satisfied so, provided ℓ_{ex} is sufficiently large

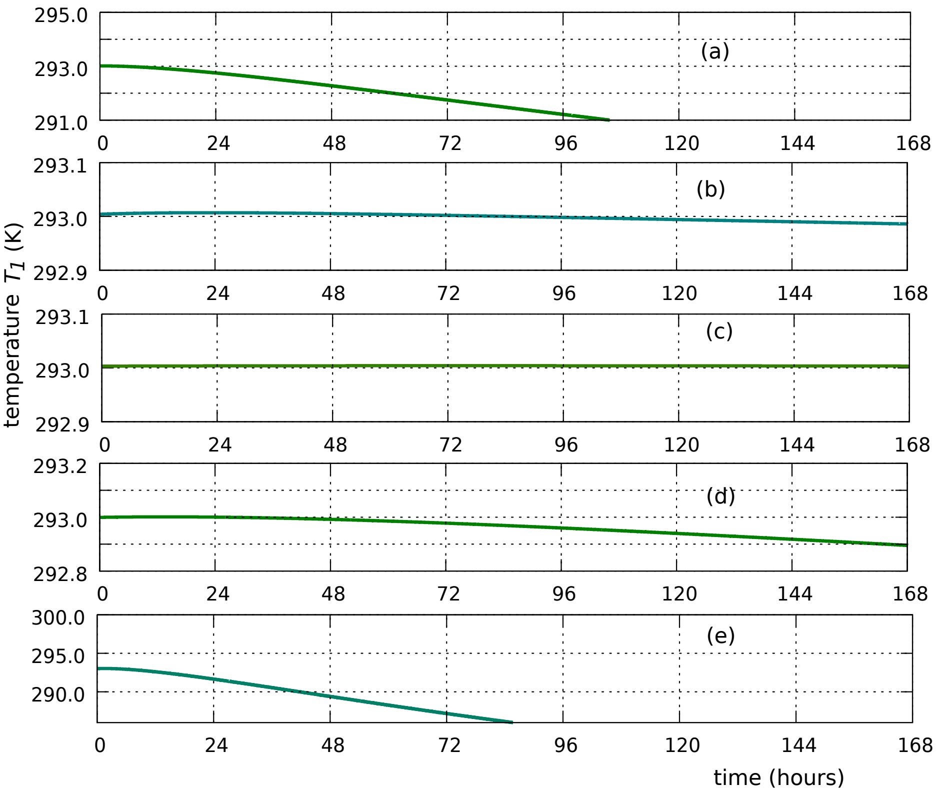

Figure 4. Numerical solutions of Eqs (1)–(4) (with $\ell_{\rm d} \to 0$, $n = m = 1$) for Endex pairs (a) 1.1c and 2.3, (b) 1.2c and 2.11, (c) 1.4c and 2.5, (d) 1.5d and 2.9, (e) 1.6 and 2.7.

we should expect $T < T_0$ for all time. This is borne out time trace in Fig. 4(a), where the temperature decreases by a detectable 1.4 K over 24 hours. It is noted that a monitored *decrease* in temperature could be a warning signal that would allow remedial actions to be carried out safely and in a timely and methodical manner, without the need to 'push the panic button'.

- # 1.2c and # 2.11: The condition $\mu \leq 1$ in the inequality relations (8) is marginally violated and stability of this system cannot be guaranteed globally. However the system remains stable, as can be seen in Fig. 4(b), apparently due to the high value of ν. The slight fall in temperature would not be detectable experimentally.
- # 1.4c and # 2.5: Here again we have an almost ideal matching Endex pair, Fig. 4(c). Note, from Table A1, that th endothermic dehydration produces HCl gas as well as steam. This could be usefully exploited in monitoring the storage system: since low levels of water vapor produced by reaction may be indistinguishable from ambient humidity, the detection of HCl could be used to activate early warning and intervention systems.
- # 1.5d and # 2.9: The condition $\nu > 1$ in the inequality relations (8) fails so we cannot guarantee the global stability of this system, Fig. 4(d). Compliance with condition $\mu < 1$ causes the temperature to fall by 0.1 K over one week, but over much longer periods of storage the temperature would begin to rise. Thus this system would be safe in a factory, where the peroxide is not stored for more than a few days before it is used, but may not be adequate for shipping bulk quantities of the peroxide across the world.
- # 1.6 and # 2.7: Apparently the extremely large value of ν overcomes the slightly non-compliant value of μ, and the temperature falls by a detectable 1 k in 24 hours, Fig. 4(d).

A more challenging and ambitious project is to Endex-stabilize a substance that decomposes in sequential stages, such as MEKP. DSC traces for MEKP clearly show decomposition occurring in three stages: the first beginning at 42°C, the second, more exothermic at onset at 83°C and the third most violent onset at 160°C (Yuan et al. 2005,

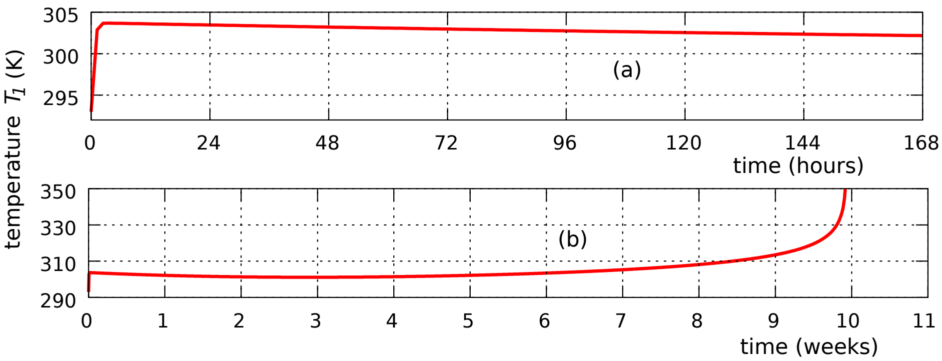

Figure 5. Numerical solutions of equations for MEKP Endex system over (a) one week and (b) 11 weeks.

Chi et al. 2009). This staged decomposition is due to the presence of two or more species in MEKP preparations, such as a monomer and dimer (Graham et al. 2011), and/or sequential decomposition reactions (Tseng et al. 2007). In this work the decomposition is modelled as a sequential process.

Endothermic reactions chosen to pair with the three stages of MEKP decomposition are listed in Table 2, along with values of the parameters. The equations for the resulting dynamical system (larger and more complicated than Eqs (1)–(4)) were integrated and the time trace is plotted in Fig. 5 (a). The temperature rises to 304 K in only 2 hours due to the first low activation energy MEKP decomposition. Why does Endex stabilization of this reaction fail? The condition $\nu > 1$ in the inequality relations (8) fails, but we saw for the reaction pair 1.5d and 2.9 that stabilization can succeed for at least a week. In this case stabilization is unsuccessful essentially because the system does not sit within the Semenov approximation, Eq. (13) and the rule of thumb Eq. (15) does not apply. As a result the MEKP is almost completely converted to the stage II reactant after 2 hours, and it is this stage II reactant that is stored at 304 K, slowly declining to 302.4 K at the end of 1 week.

For the MEKP stage II-2.11 reaction pair the condition $\nu > 1$ fails badly, and one could predict that at some point the system may undego thermal runaway. This is borne out by the numerical data plotted in Fig. 5 (b): after 9 weeks the temperature runs out of control, and from the datafile this is entirely due to the MEKP stage II decomposition, since the stage III reactant is still accumulating.

So Endex stabilization of MEKP is still a problem, (a) because it is difficult to suppress the initial low temperature, low enthalpy reaction, and (b) thermokinetic data for more hydrated metal salt dehydrations are needed in order to find a better match for the stage II decomposition. It is not generally acceptable to allow the stage I decomposition to proceed and store the substance at ∼304 K. However it may be possible to find a matching metal salt dehydration for stage II that brings the temperature down to an acceptable level.

4 Discussion and conclusions

Since nearly 25% of all chemical accidents are traced to inappropriate storage conditions (Weisenburger and Vogt 2008), there is an unmet need for new storage solutions for thermally hazardous substances. Such chemicals are often stored/transported in drums or barrels in a room or container, which may be refrigerated, and the thermal hazards of such arrangements have been investigated by Gray (2001). The solution proposed in this work is inherent Endex stabilization using the dehydrations of metal salts. The overall Endex system is adiabatic, which has the advantage that external heat sources are excluded.

The main result of this work is that Endex stabilization of rogue or runaway exothermic reactions in storage tanks is both possible and feasible. For an adiabatic Endex storage system with good inter-segment thermal conductance, the conditions (8) have been derived rigorously for which all thermal excursions are forbidden and the system is intrinsically safe.

Several industrial organic peroxides that are known to undergo violently exothermic thermal decomposition were matched individually with hydrated metal salts that undergo endothermic dehydrations. Although in most cases thermokinetic matching is imperfect and the conditions (8) are partially violated, numerical simulations show that Endex stabilization is effective over a period of at least one week.

Table A1. Compilation of experimental thermokinetic data for endothermic dehydrations of hydrated metal salts.

#	Reaction	A (s^{-1}), E (kJ/mol)	ΔH (J/g), Temp. range (K)	References
2.1	$Mg(CH_3COO)_2 \cdot 4H_2O \rightarrow Mg(CH_3COO)_2$	4.17×10^{20}, 152	not given, 318–398	Mu and Perlmutter (1981)
2.2	$Zn(COOH)_2.2H_2O \rightarrow Zn(COOH)_2$	4.66×10^{19}, 160	597.2, 358–393	Mu and Perlmutter (1981), Zhang et al. (2008)
2.3	$2NaHCO_3 \rightarrow Na_2CO_3$	1.158×10^{10}, 101.1	806.6, 353–433	Hartman et al. (2013)
2.4	$MgSO_4 \cdot 7H_2O \rightarrow MgSO_4 \cdot H_2O$	4.90×10^{8}, 60	1079, 298–473	Ruiz-Agudo et al. (2007)
2.5	$2AlCl_3 \cdot 6H_2O \rightarrow Al_2O_3 \cdot 2HCl \cdot 2H_2O + 4HCl + 7H_2O$	1.61×10^{14}, 135.9	1500, 363–523	Hartman et al. (2005)
2.6	$Na_2CO_3 \cdot 10H_2O \rightarrow Na_2CO_3 \cdot H_2O + 9H_2O$	1.355×10^{11}, 82.14	1656, 292–333	Hartman et al. (2001)
2.7	$Na_2CO_3 \cdot H_2O \rightarrow Na_2CO_3 + H_2O$	5.963×10^{15}, 121.5	473.6, 338–360	Hartman et al. (2001)
2.8	$ZnSO_4 \cdot 7H_2O \rightarrow ZnSO_4 \cdot 6H_2O + H_2O$	3.067×10^{5}, 55	217.0[a], 293–380	Straszko et al. (1997)
2.9	$ZnSO_4 \cdot 6H_2O \rightarrow ZnSO_4 \cdot H_2O + 5H_2O$	7.38×10^{15}, 139	1018.5[a], 375–460	Straszko et al. (1997)
2.10	$Al_2(SO_4)_3 \cdot 18H_2O$ dehydrations			
	Stage I	8.25×10^{4}, 45.10	218.9, 325–354	Chou and Soong (1984), Çilgi and Cetişli (2009)
	Stage II	1.19×10^{5}, 54.68	1120, 354–437	Chou and Soong (1984), Çilgi and Cetişli (2009)
	Stage III	1.09×10^{7}, 94.9	not given, 437–580	Chou and Soong (1984), Çilgi and Cetişli (2009)
2.11	$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$	6.60×10^{11}, 118.0	310, 399–469	Lozano et al. (1989)

[a] Estimated from data given in Wagman et al. (1982).

The most difficult case is that of MEKP, which both undergoes a low temperature, weakly exothermic decomposition *and* several sequential thermal decompositions. Endex suppression of the stage I reaction fails because the inter-segment thermal conductance is inadequate, i.e., the reaction sits outside the Semenov approximation. Stabilization of stage II can be successful for some time, but ultimately thermal runaway occurs because the reaction frequency matching is poor.

As well as demonstrating the potential of Endex storage systems for safe storage of explosive and dangerous substances, this work also shows up a need to obtain experimental kinetic data for more metal salt dehydration reactions and improved understanding of multistage peroxide decompositions. A particular proposed Endex storage system should be tested experimentally before implementation. Finally, I emphasize again the need to provide pressure venting for endothermic segments containing hydrated metal salts.

Appendix

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Table A2. Compilation of experimental kinetic parameters and decomposition enthalpies for various industrial peroxides. CHP cumene hydroperoxide, DCP dicumyl peroxide, DP diethyl peroxide, DTBP di-*tert*-butyl peroxide, TBPB *tert*-butyl peroxybenzoate, MEKP methyl ethyl ketone peroxide, TBEH *tert*-butyl peroxy 2-ethyl hexanoate.

#	Peroxide	A (s^{-1}), E (kJ/mol)	$-\Delta H$ (J/g), Temp. range (K)	Reference
1.1a	CHP	2.0×10^9, 102	1538, 373–483	Ben Talouba et al. (2011)
1.1b	CHP	1.33×10^{11}, 125	1810, 373–479	Duh et al. (1998)
1.1c	CHP	$1.61 \times 10^{11\,\mathrm{a}}$, 125	1810, 353–488	Luo et al. (2001)
1.1d	CHP	9.57×10^{12}, 108	1283, 397–424	Liu et al. (2011)
1.2a	DCP	1.2×10^{10}, 135	861.5, 393–493	Ben Talouba et al. (2011)
1.2b	DCP	1.1×10^{13}, 132	741, 383–453	Wu and Shu (2010)
1.2c	DCP	2.0×10^{11}, 117	736, 383–443	Shen et al. (2010)
1.3	DP (gas)	1.58×10^{14}, 148	2186, 451–495	Fine et al. (1970)
1.4a	DTBP	1.36×10^{18}, 117	897, 393–462	Liu et al. (2011)
1.4b	DTBP	1.57×10^{10}, 109	1106, 408–483	Tseng and Lin (2011)
1.4c	DTBP	5.32×10^{13}, 134.58	1100, 371–433	Chu et al. (2011)
1.5a	TBPB	5.3×10^{13}, 127.8	1411, 380–430	Verhoeff and van den Berg (1984)
1.5b	TBPB	6.31×10^{14}, 116	1209, 354–428	Liu et al. (2011)
1.5c	TBPB	2.62×10^{11}, 111.7	1266, 338–438	Lin et al. (2010)
1.5d	TBPB	1.17×10^{16}, 145.6	1250, 353–383	Hordijk and de Groot (1986)
1.6	TBEH	4.81×10^{13}, 120.8	1140, 310–405	Hordijk and de Groot (1986)
1.7a	MEKP$^{\mathrm{b}}$	5.07×10^5, 49.8	321–345	Fu et al. (2003)
1.7b	MEKP			
	Stage I	2.24×10^5, 49.2	53.69, 303–348	Yuan et al. (2005), Chi et al. (2009)
	Stage II	1.0×10^{13}, 117.7	483.2, 356–433	Yuan et al. (2005), Chi et al. (2009)
	Stage III	3.5×10^{19}, 168	768, 433–483	Yuan et al. (2005), Chi et al. (2009)

[b] With 1% H_2SO_4.

References

Ball, R., 2011. Oscillatory thermal instability and the Bhopal disaster. *Process Saf. Environ. Protect.* 89: 317–322.

Ball, R., 2013a. Entropy generation analyses of Endex and conventional calcium looping processes for CO_2 capture. Fuel (In press).

Ball, R., 2013b. Thermal oscillations in the decomposition of organic peroxides: identification of a hazard, utilization, and suppression. *Ind. Eng. Chem. Res.* 52: 922–933.

Ball, R., Gray, B. F., 1999. Thermal stabilization of chemical reactors. II. Bifurcation analysis of the Endex reactor. *Proc. R. Soc. Lond. A* 455: 4223–4243.

Ben Talouba, I., Balland, L., Mouhab, N., Abdelghani-Idrissi, M. A., 2011. Kinetic parameter estimation for decomposition of organic peroxides by means of DSC measurements. *J. Loss Prevent. Process Ind.* 24: 391–396.

Çilgi, G. K., Cetişli, H., 2009. Thermal decomposition kinetics of aluminum sulfate hydrate. *J. Therm. Anal. Calorim.* 98: 855–861.

Chi, J.-H., Wu, S.-H., Shu, C.-M., 2009. Thermal explosion analysis of methyl ethyl ketone peroxide by non-isothermal and isothermal calorimetric applications. *J. Hazard. Mater.* 171: 1145–1149.

Chou, K.-S., Soong, C.-S., 1984. Kinetics of the multistage dehydration of aluminium sulfate hydrate. *Thermochimica Acta* 81: 305–310.

Chu, Y. C., Chen, J. R., Tseng, J. M., Tsai, L. C., Shu, C. M., 2011. Evaluation of runaway thermal reactions of di-tert-butyl peroxide employing calorimetric approaches. *J. Therm. Anal. Calorim.* 106: 227–234.

Căilean, A.-D., Mateescu, T., Yalewski, L., 2011. Determination of termo-physical properties of a phase-change material. *Buletinul Institutului Politehnic din Iaşi* LVII: 87–94.

Duh, Y.-S., Kao, C.-S., Hwang, H.-H., Lee, W. W.-L., 1998. Thermal decomposition kinetics of cumene hydroperoxide. *Trans. IChemE* 76B: 271–276.

Fine, D. H., Gray, P., MacKinven, R., 1970. Thermal effects accompanying spontaneous ignitions in gases. III. The explosive decomposition of diethyl peroxide. *Proc. R. Soc. Lond. A* 316: 255–268.

Fu, Z.-M., Li, X.-R., Koseki, H., Mok, Y.-S., 2003. Evaluation on thermal hazard of methyl ethyl ketone peroxide by using adiabatic method. *J. Loss Prevent. Process Ind.* 16: 389–393.

Graham, S. R., Hodgson, R., Vechot, L., Iqbal Essa, M., 2011. Calorimetric studies on the thermal stability of methyl ethyl ketone peroxide (MEKP) formulations. *Process Saf. Environ. Protect.* 89: 424–433.

Gray, B. F., Ball, R., 1999. Thermal stabilization of chemical reactors. I. The mathematical description of the Endex reactor. *Proc. R. Soc. Lond. A* 455: 163–182.

Gray, B. F., Macaskill, C., 2004. The role of self-heating in the estimation of kinetic constants for thermally unstable materials using differential scanning calorimetry (DSC). In: Grayson, S. J. (Ed.), INTERFLAM 2004: Proc. 10th international conference. Interscience Communication, London, UK, pp. 961–973.

Hartman, M., Svoboda, K., Pohořely, M., Šyc, M., 2013. Thermal decomposition of sodium hydrogen carbonate and textural features of its calcines. *Ind. Eng. Chem. Res.* 52: 10619–10626.

Hartman, M., Trnka, O., Veselý, V., Svoboda, K., 2001. Thermal dehydration of the sodium carbonate hydrates. *Chem. Eng. Com.* 185: 1–16.

Hartman, M., Šolcová, O., Trnka, O., 2005. Thermal decomposition of aluminum chloride hexahydrate. *Ind. Eng. Chem. Res.* 44: 6591–6598. 10.1021/ie058005y.

Ho, T.-C., Duh, Y.-S., 1998. Case studies of incidents in runaway reactions and emergency relief. *Process Saf. Prog.* 17: 259–262.

Hordijk, A. C., de Groot, J. J., 1986. Experimental data on the thermal kinetics of organic peroxides. *Thermochimica Acta* 101: 45–63.

Kotoyori, T., 1995. Critical temperatures for the thermal explosion of liquid organic peroxides. *Proc. Saf. Prog.* 14: 37–44.

Lin, C.-P., Tseng, J.-M., Chang, Y.-M., Liu, S.-H., Cheng, Y.-C., Shu, C.-M., 2010. Modeling liquid thermal explosion reactor containing *tert*-butyl peroxybenzoate. *J Therm. Anal. Calorim.* 102: 587–595.

Liu, S.-H., Lin, C.-P., Shu, C.-M., 2011. Thermokinetic parameters and thermal hazard evaluation for three organic peroxides by DSC and TAM III. *J. Ther. Anal. Calorim.* 106: 165–172.

Lozano, R., Roman, J., de Jesus, F., 1989. Kinetic studies by DSC on the thermal decomposition of calcium oxalate. *Thermochimica Acta* 143: 93–100.

Luo, K.-M., Chang, J.-G., Lin, S.-H., Chang, C.-T., Yeh, T.-F., Hu, K.-H., Kao, C.-S., 2001. The criterion of critical runaway and stable temperatures in cumene hydroperoxide reaction. *J. Loss Prevent. Process Ind.* 14: 229–239.

Mu, J., Perlmutter, D. D., 1981. Thermal-decomposition of carbonates, carboxylates, oxalates, acetates, formates, and hydroxides. *Thermochimica Acta* 49: 207–218.

Ruiz-Agudo, E., Martin-Ramos, J. D., Rodriguez-Navarro, C., 2007. Mechanism and kinetics of dehydration of epsomite crystals formed in the presence of organic additives. *J. Phys.l Chem. B* 111: 41–52.

Shen, S.-J., Wu, S.-H., Chi, J.-H., Wang, Y.-W., Shu, C.-M., 2010. Thermal explosion simulation and incompatible reaction of dicumyl peroxide by calorimetric technique. *J. Therm. Anal. Calorim.* 102: 569–577.

Straszko, J., Olszak-Humienik, M., Możejko, J., 1997. Kinetics of thermal decomposition of $ZnSO_4 \cdot 7H_2O$. *Thermochimica Acta* 292: 145–150.

Tseng, J.-M., Chang, Y.-Y., Su, T.-S., Shu, C.-M., 2007. Study of thermal decomposition of methyl ethyl ketone peroxide using DSC and simulation. *J. Hazard. Mater.* 142: 765–770.

Tseng, J.-M., Lin, C.-P., 2011. Green thermal analysis technology for evaluating the thermal hazard of di-*tert*-butyl peroxide. *Ind. Eng. Chem. Res.* 50: 9487–9494.

Verhoeff, J., van den Berg, P. J., 1984. Thermal runaway in the thermal explosion of a liquid. *J. Therm. Anal.* 29: 533–551.

Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., 1982. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units. *J. Phys. Chem. Ref. Data* 11: Suppl. 2.

Wu, S.-H., Shu, C.-M., February 2010. Reactive hazard analysis of cumene hydroperoxide and dicumyl hydroperoxide. *Process Saf. Prog.* 29: 162–165.

Yuan, M.-H., Shu, C.-M., Kossoy, A. A., 2005. Kinetics and hazards of thermal decomposition of methyl ethyl ketone peroxide by DSC. *Thermochimica Acta* 430: 67–71.

Zhang, J., Liu, Y. Y., Zeng, J. L., Xu, F., Sun, L. X., You, W. S., Sawada, Y., 2008. Thermodynamic properties and thermal stability of the synthetic zinc formate dihydrate. *J. Therm. Anal. Calorim.* 91: 861–866.

Weisenburger, G. A., Vogt, P. F., 2008. Safety Notables: Information from the Literature. *Org. Process Res. Dev.* 12: 1277–1282.

Gray, B. F., 2001. On the critical conditions for an assembly of interacting thermons. *ANZIAM J.* 43:1–11.